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AN EXAMINATION OF THE PETROPORPHYRINS FOUND IN OIL SHALE FROM
THE JULIA CREEK DEPOSIT OF THE TOOLEBUC FORMATION

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INTRODUCTION

The nature of the petroporphyrins found in a variety of crude oils, oil shales, ancient and recent sediments have been a subject of continual interest since these compounds were first isolated from such materials by Treibs et al. (1) some fifty years ago. It is now generally agreed (2) that the petroporphyrins represent the degradation products of chlorophyll and that they consist predominantly of homologous series of deoxophylloerythroetioporphyrin (DPEP) and etio porphyrins. However, as yet unidentified porphyrin compounds which do not belong to either of these two classes have been observed (3) in some samples and the proposition that all petroporphyrins are derived from chlorophyll has also been questioned (4).

The oil shale of the Toolebuc formation in Queensland, Australia has been shown (5) to contain relatively high concentrations of vanadium and nickel porphyrin compounds. Saxby et al. (5) have suggested that these porphyrins are largely of the DPEP and etio-type and also observed significant variations in their concentrations in samples taken from various sites in the deposit. In this paper we describe two further aspects of the porphyrin compounds in this deposit. First, the variations in the concentrations of the chloroform extractable metal porphyrin compounds through well-characterized drill cores was determined, and second, the nature of the vanadium porphyrins was examined using absorption spectrophotometry and insertion probe, fast atom bombardment (FAB) and field desorption (FD) mass spectrometry techniques.

EXPERIMENTAL

Samples of the drill cores from the Julia Creek deposit used were ground and sieved, the -90 μ m fraction being used. Samples of 15-20 g were exhaustively extracted with chloroform in soxhlet extractors. As illustrated in Figure 1, the extract was filtered through a Millipore filter, and analyzed for V, Ni, Fe, Cu and Cr. Atomic absorption, inductively-coupled plasma emission and X-ray fluorescence spectrometry were used to analyze both the extracts and the raw shale.

The separation of the extract into polycyclic hydrocarbons, nickel and vanadium porphyrin fractions was accomplished using $\text{CCl}_4/\text{CHCl}_3$ chromatography with Kieselgel (Merck). The vanadium porphyrin fraction was then further separated into seven fractions using a variety of column chromatography procedures to be described in detail elsewhere (6). Fraction 3 was the predominant one, and comprised approximately 50-60% of the total vanadium porphyrins present. Demetallation of the porphyrin fractions was carried out with methanesulfonic acid (Merck) using published procedures (7).

UV-visible spectra were obtained using a Cary 118C spectrophotometer. Insertion-probe mass spectra were obtained with a Dupont 21-491B mass spectrometer, the FAB spectra with a VG MM-ZAB instrument, and the FD spectra with a JEOL DX-300 mass spectrometer. High pressure liquid chromatography measurements were made with a Waters instrument fitted with dual channel (405 and 546 nm) optical detection and C18 columns.

RESULTS AND DISCUSSION

Table I summarizes the concentrations of trace elements extracted with chloroform from two oil shale samples of the drill cores. Although vanadium is clearly the major element present in the form of metal-organic complexes, significant concentrations of compounds containing nickel, iron, copper and chromium are similarly extracted. As will be shown below, the nickel and vanadium appear to be present largely as porphyrin complexes, but it has not been possible to demonstrate that elements such as iron and copper are also present as porphyrins or as some other form of metal-organic complex.

TABLE I
METAL-ORGANIC COMPLEXES EXTRACTABLE WITH CHLOROFORM FROM
JULIA CREEK SHALE

Element	Concentration Extracted $\mu\text{g g}^{-1}$	
	Sample 1	Sample 2
	Oil Shale, Deep Core 90-92 m	Oil Shale, Shallow Core 31-33 m
Vanadium	104.0	27.0
Nickel	6.0	4.0
Iron	3.0	7.0
Copper	0.26	0.74
Chromium	1.0	0.13
Molybdenum	0.26	0.43
Manganese	0.09	0.09
Magnesium	0.30	0.06
Zinc	0.39	0.20

Variations in the total (i.e. organic and inorganic) concentrations of vanadium, nickel, iron and copper and of the chloroform extractable forms of these elements through the two drill cores are summarized in Figure 2. These results demonstrate the preferential concentration of the chloroform extractable forms of these elements in coquinite and particularly the oil shale segments of the two cores, and the virtually complete absence of these compounds in the mudstone underlying and overlying the deposit. It is also apparent that there are significant differences in the concentrations of the organic forms of these elements within the coquinite and oil shale layers. Indeed, the variations in the soluble organic vanadium concentrations within the individual drill cores are comparable to the variations found in samples from widely different locations of the Toolebuc formation (5). It is also interesting to note that the variation with depth in the cores of the concentrations of the chloroform-soluble forms of vanadium, nickel, iron and copper are significantly different from each other. This observation may indicate that the various metal ions are complexed by different types of organic ligands, and, as indicated below, some evidence was obtained that the porphyrins complexed to the nickel ion are different from those complexed to the vanadyl ion.

Although there are obvious differences in the concentrations of the organic vanadium complexes found in the shallow and deep drill cores, the nature of the vanadium complexes present appears to be virtually identical, as shown (Figure 3) by the HPLC of the vanadium porphyrin fractions from core samples taken at depths of 90-92 m and 29-31 m. It would clearly be desirable to extend such studies to samples taken from much greater depths in the Toolebuc formation.

As indicated in Figure 1, it was possible to separate the vanadium porphyrins extracted from the oil shale (90-92 m) into several distinct fractions using column chromatography. XRF analysis of these fractions showed that all were vanadium complexes and none were found to contain any measureable concentrations of iron, nickel or copper. Comparison of the uv-visible absorption spectra of these fractions (Figure 4) with the spectra of known vanadium chlorin, phylloerythrin and DPEP complexes (8), suggest that fractions 422 and 442 with absorption maxima at 600 nm were probably vanadium phylloerythrin complexes. These two fractions do not appear to be identical to the rhodo-type petroporphyrins with an absorption maximum at 590 nm isolated by Millson et al. (9) and discussed in detail by Bakér et al. (10) because of the significant difference in the absorption spectra. Also, as will be shown below, the mass spectra of fractions 422 and 442 are more complex than would be expected for the rhodo-type porphyrin. Sample 630 may be vanadium chlorin derivative, while the spectra of fractions 3, 61, 41 and 441 were typical of vanadium porphyrins with maxima at 412, 538 and 575 nm. However, the ratios of the intensities of the 575 and 538 nm absorption bands, which are in the range 1.15-1.20 for these samples, appear to be more consistent with deoxophylloerythrin derivatives rather than the DPEP derivatives. No fraction having a spectrum similar to that shown by Hodgson and Baker (8) for the vanadyl-DPEP complex could be isolated from the present samples.

Insertion-probe mass spectra were obtained for these fractions using both EI and CI ionization, typical results being shown in Figure 5. The spectra obtained using these two ionization modes were similar except that the peaks in the CI spectra were located, as expected, one mass unit higher than the corresponding EI peaks. The sequence of peaks at $m/e = 513, 527, 541$ and 555 observed for sample 3 are typical of vanadyl-DPEP homologues. The insertion-probe spectra of samples 422 and 442 were, surprisingly, virtually identical to those of fraction 3, even though the former two compounds were clearly not vanadyl DPEP derivatives. The mass spectra of samples 61, 441 and 421, which all have typical vanadyl porphyrin visible spectra, showed prominent even mass number peaks at $m/e = 526, 540$ and 554 . Similar observations have been made by Blumer

and Rudrum (11) and are attributed to the effects of the pyrolysis of the sample in probe.

It was also possible to obtain FAB mass spectra of several of the porphyrin fractions. The most notable difference in the insertion probe and FAB spectra were obtained for sample 441 (Figure 6) for which the FAB spectra showed not only a completely different distribution of peaks in the mass range 500-600 amu, but also yielded a second set of prominent peaks in the range 1022-1078 amu. Particularly prominent in this spectrum was the series 495, 509, 523, 537, 551 and 565 i. e. $(541-4) + 14n$; which presumably indicates the presence of unsaturated substituent groups on the porphyrin ring. The high molecular weight peaks appear in a mass range corresponding to 35-40 carbon atoms additional to those of the basic DPEP structure. These compounds are thus superficially similar to the high molecular weight vanadium porphyrins isolated by Blumer et al. (11).

The FAB spectra of the two phylloerythrin fractions (sample 422 and 4422) also showed significant differences from the insertion probe spectra (Figure 6). FAB spectra of samples 4422, 422 and 61 also showed peaks in the range 1000-1200 amu, but these were not as clear as those observed for sample 422, and further work would be required to confirm their presence. The low molecular weight spectra were again dominated by peaks corresponding to $(541-2) + 14n$ and $(541-4) + 14$ indicative of some degree of unsaturation in the substituent groups. These two sequences appear to be similar to those of an as yet unidentified series reported by Thomas and Blumer (3).

The HPLC (C18 Bondapak semipreparative column, methanol 0.5 cc/min) of sample 3 showed seven major and well-separated peaks, of which peaks 4, 5 and 7 were predominant. Fractions containing these peaks were collected as they eluted from the column and examined by FD mass spectrometry. All fractions had UV-visible spectra typical of vanadium porphyrin complexes. As shown in Figure 7, relatively simple mass spectra were obtained. Peak 1 appears to consist of two etio homologues at $m/e = 515$ and 501 , while peaks 2, 3 and 4 are consistent with compounds of the DPEP series. Peaks 5 and 7 show identical mass spectra consistent with a DPEP-2 series but are surprisingly separated by peak 6 which appears to be a mixture of the DPEP (527, 541, 555, 569, 583 and 599) series and DPEP-2 (553, 567) series. To a first approximation, these compounds would be expected to be eluted in order of decreasing polarity of this reverse phase column, and it is difficult to interpret these results without postulating that several compounds having molecular weights corresponding to the DPEP series but of significantly different chemical constitution are present in the samples.

Attempts to demetallate the various porphyrin fractions appeared to be completely successful only in the case of the nickel porphyrins and for sample 3, while demetallation of samples 630, 442 and 4422 yielded no porphyrin type compounds at all. HPLC runs on the demetallated nickel porphyrins and the vanadium porphyrins from fraction 3 showed these to be significantly different. Similar observations have been made previously (12) and may explain why the nickel and vanadium porphyrins appear to have different distributions in the drill cores. However, because of the possibility of decomposition of the porphyrins during demetallation, these observations are far from conclusive.

In conclusion, it should be noted that this investigation described only preliminary attempts to identify some of the porphyrinic compounds present in what appears to be an exceedingly complex mixture in the oil shale of the Toolebuc formation. The possible presence of significant concentrations of chlorin and phylloerythrin type compounds in this shale suggests that the deposit has undergone very little maturation, and a more complete identification of the compounds present should assist in developing a clearer understanding of the origin and of the reactions of petroporphyrins in a geological environment.

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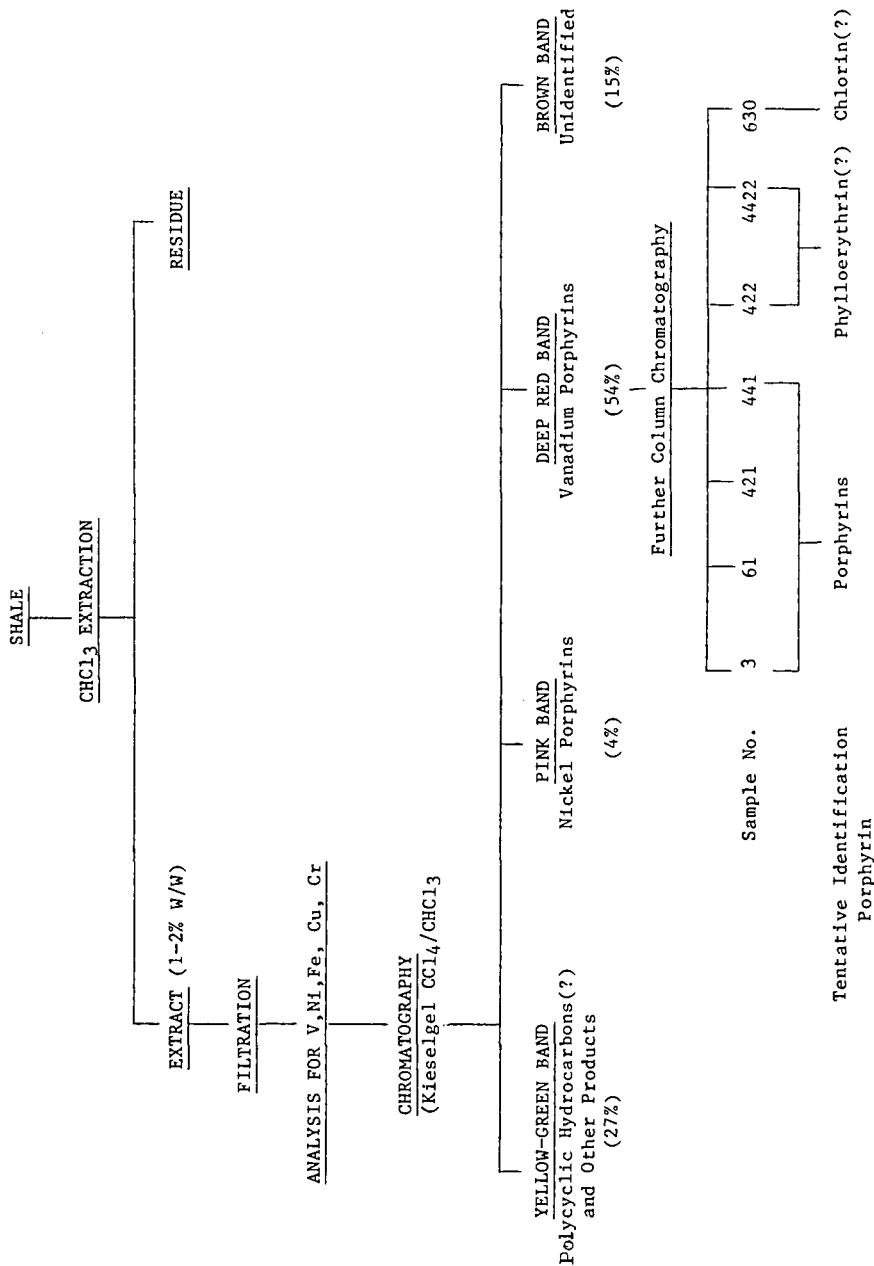


Figure 1. Schematic outline of the separation procedures used in this work.

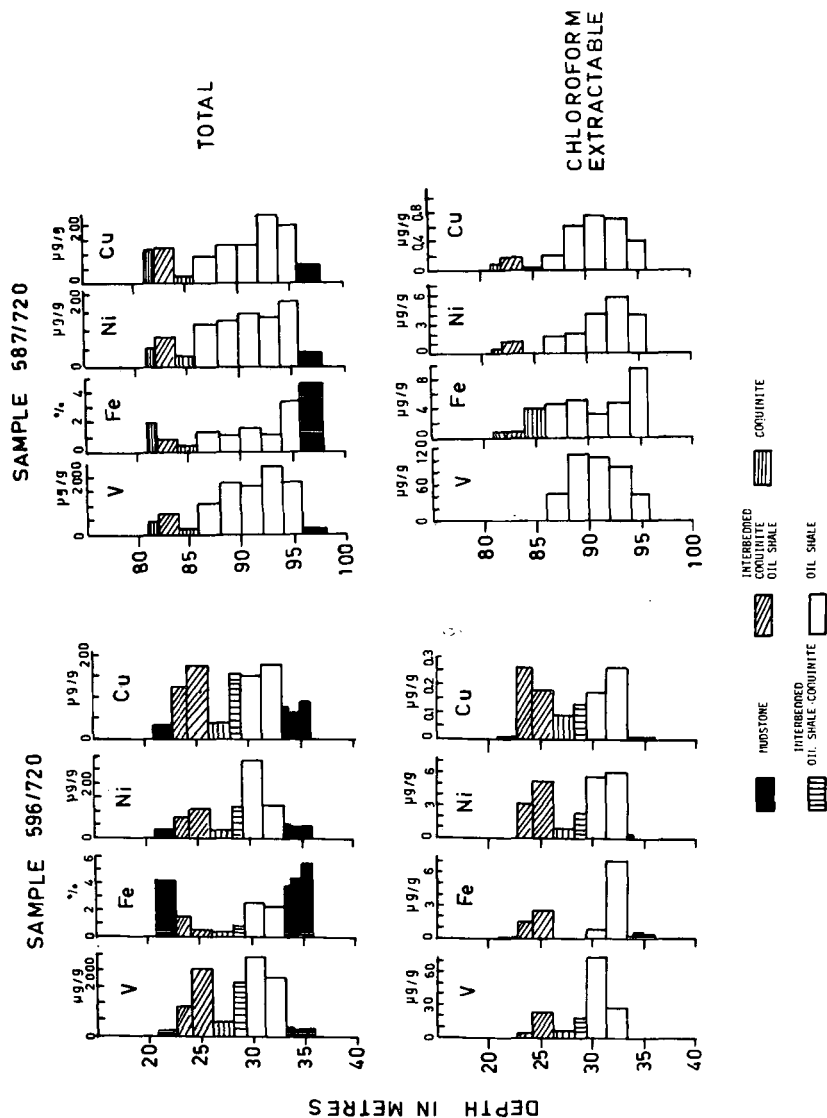


Figure 2. Distribution of the total (upper diagram) and chloroform extractable (lower diagram) concentrations of vanadium, iron, nickel and copper in two drill cores from the Julia Creek deposit.

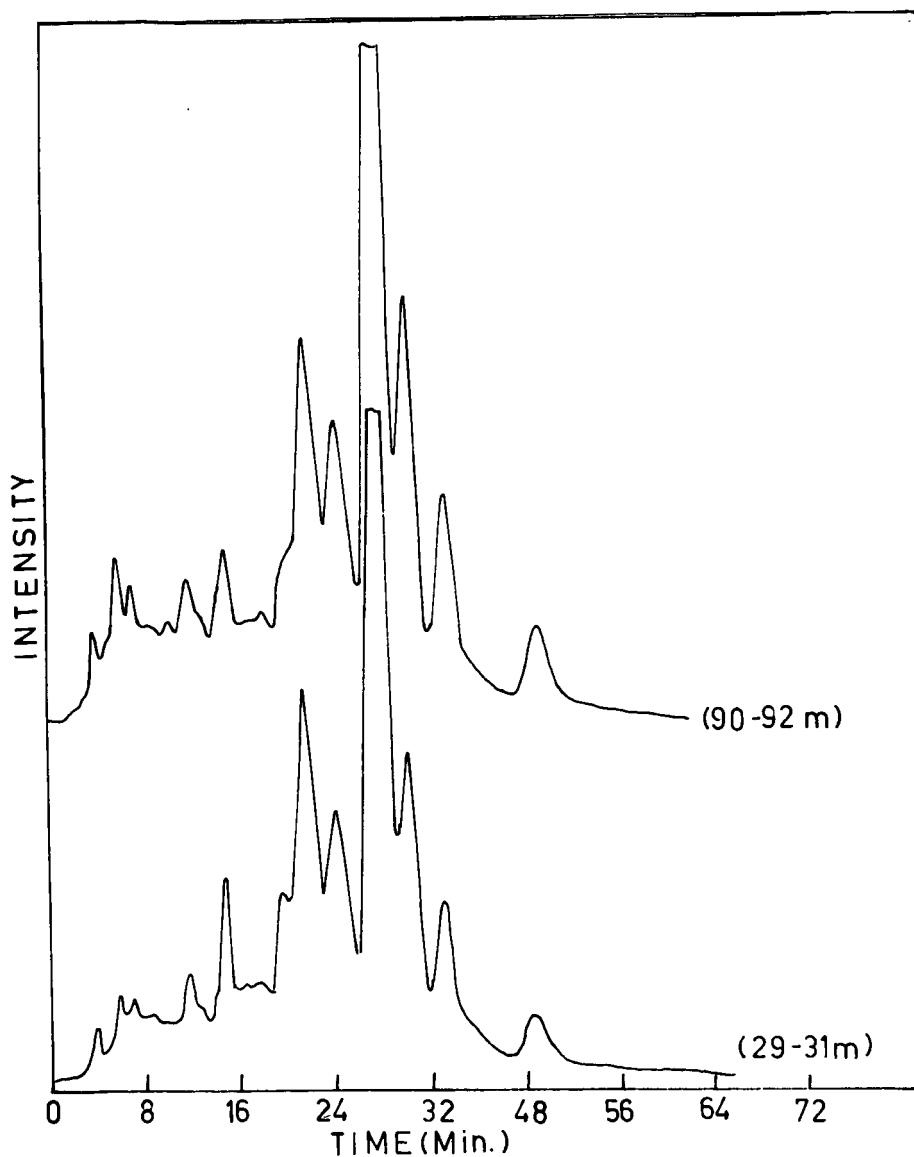


Figure 3. HPLC of the chloroform extracts from samples of oil shale at depths of 90-92 m and 29-31 m. C₁₈ column, methanol 2 cc/min.

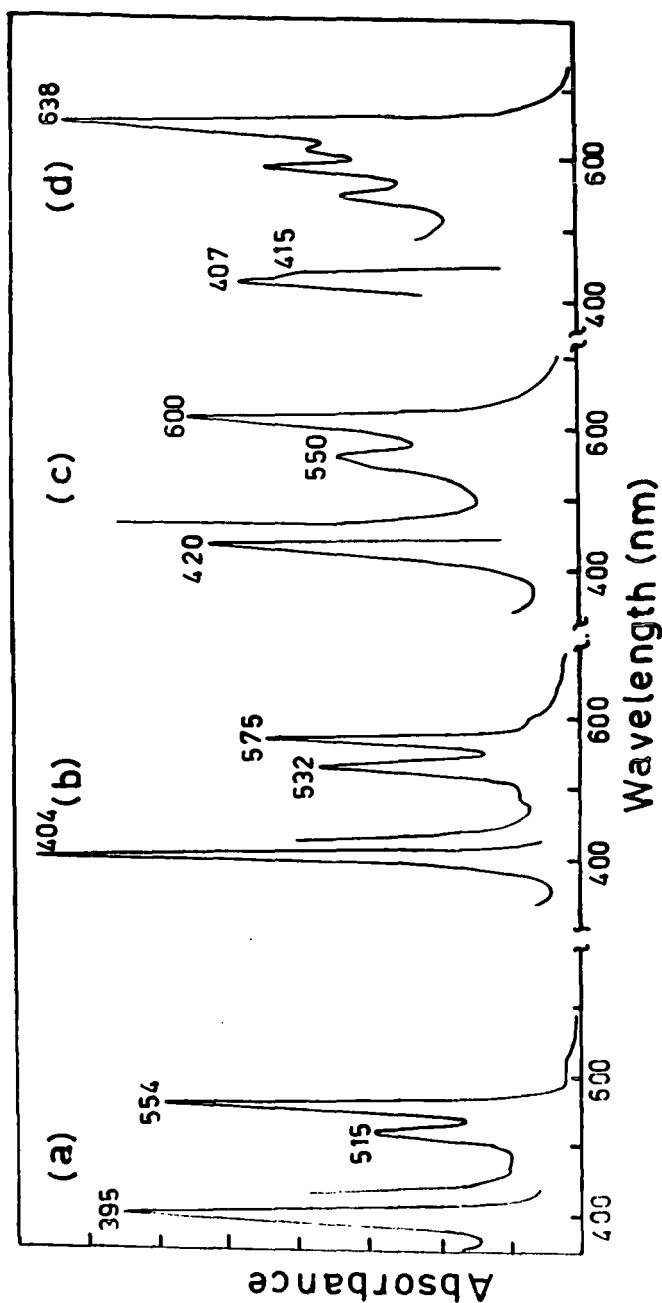


Figure 4. Typical absorption spectra of the various porphyrin fractions determined in chloroform solution. (a):- spectrum of nickel porphyrin fraction, (b) spectrum typical of fractions 3, 61, 421 and 441 and identified as vanadyl porphyrins, (c) spectrum typical of fractions 422 and 4422, tentatively identified as vanadyl phylloerythrin derivatives and (d) spectrum of fraction 630; possibly a vanadyl-chlorin complex. This sample contained some vanadyl porphyrin impurities as shown by the absorption peaks at 407, 575 and 533 nm.

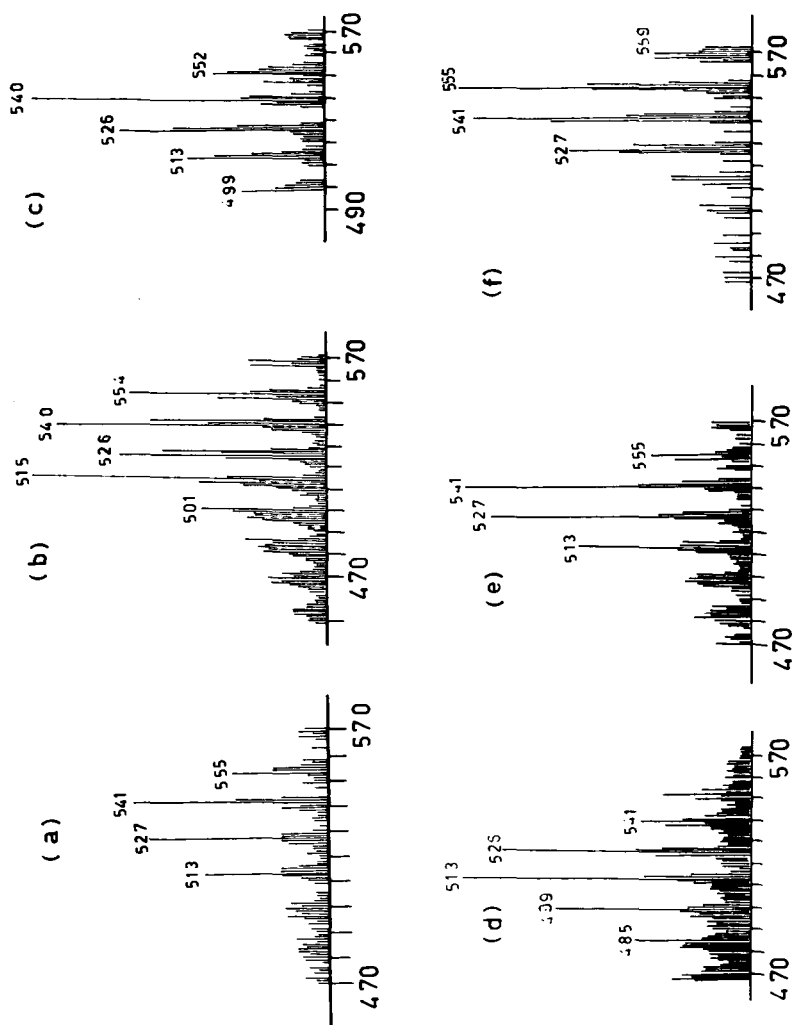


Figure 5. Insertion-probe mass spectra (EI) of various porphyrin fractions. (a) Sample 3, (b) Sample 61, (c) Sample 441, (d) Sample 421, (e) Sample 422, (f) Sample 442.

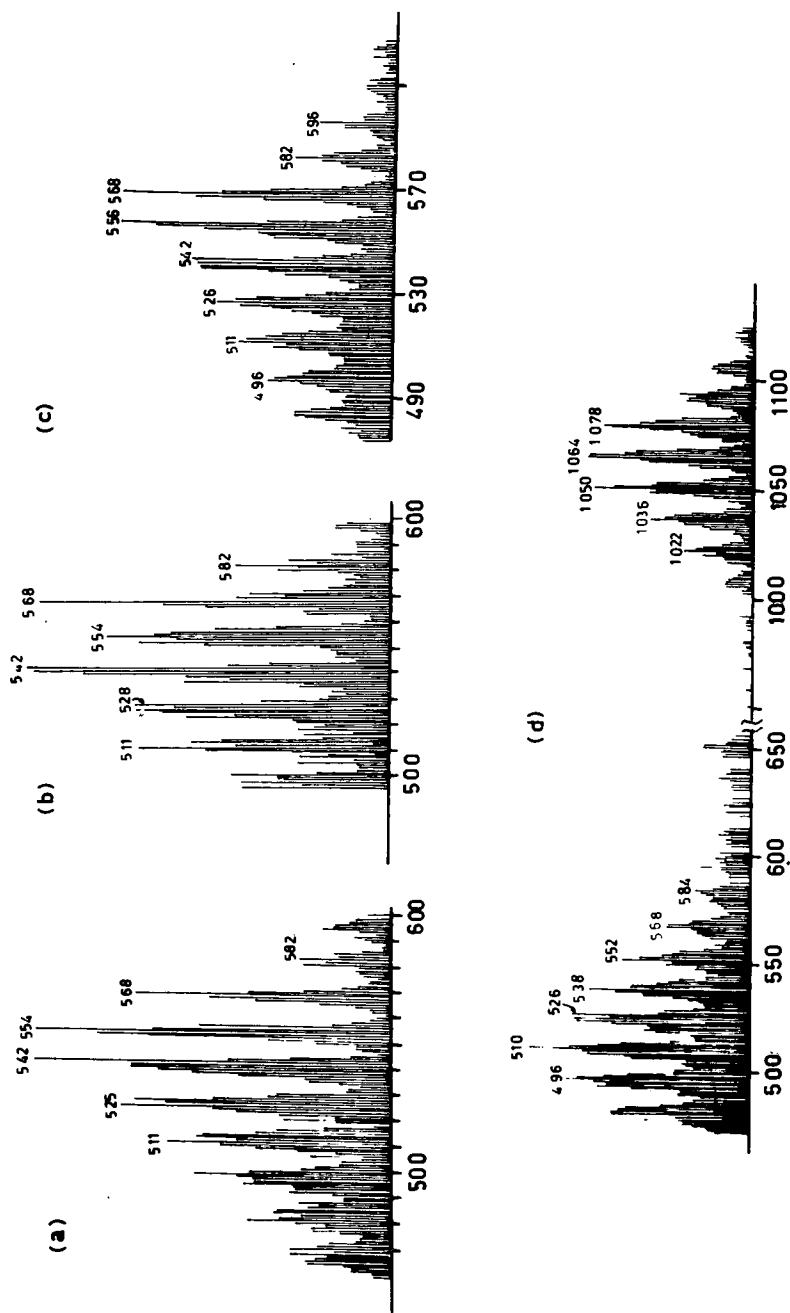


Figure 6. FAB spectra (EI) of various porphyrin fractions. (a) Sample 61, (b) Sample 4422, (c) Sample 422, and (d) Sample 441. The parent peaks would appear as $[M + H]^+$ ions.

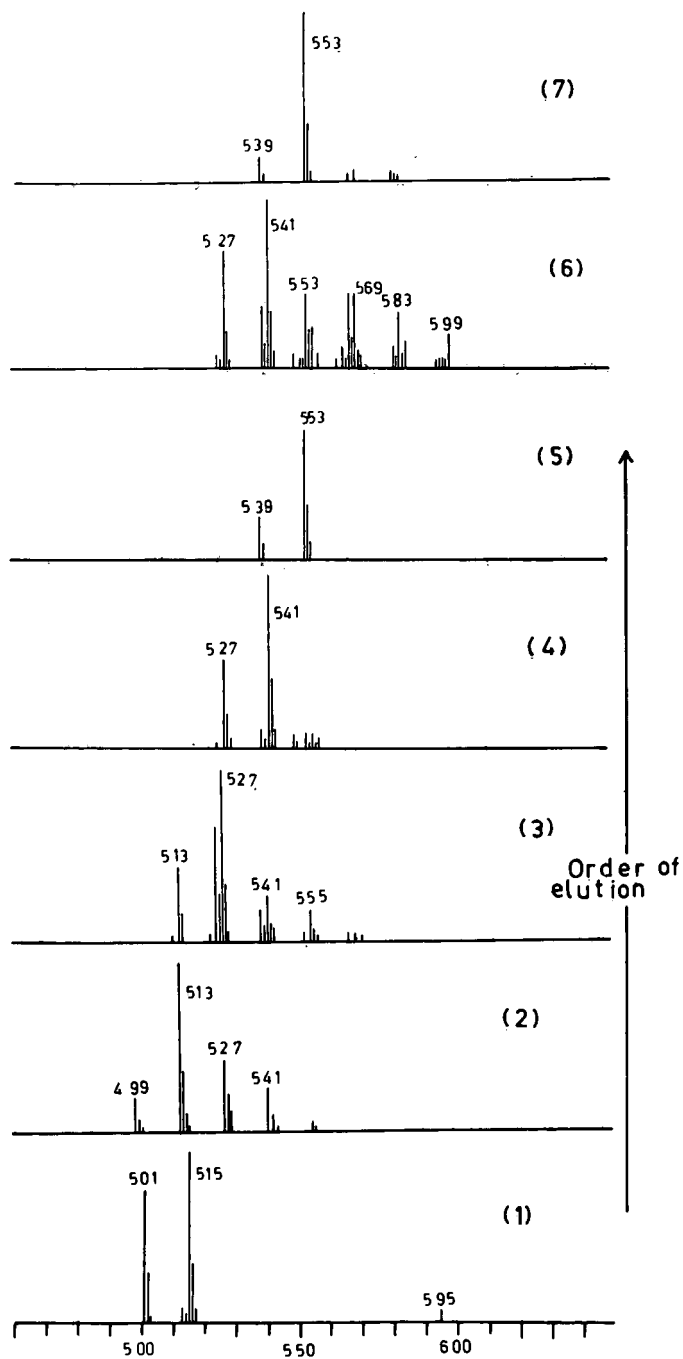


Figure 7. FD mass spectra of the seven major fractions found by HPLC in Sample 3.

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